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Shape memory effect in thermal retraction of polyethylene

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21 settembre 2012

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- ✓ introduction
- ✓ thermo-retraction and shape memory
- ✓ the model
- ✓ comparison with experimental results
- ✓ conclusions

Shape memory effect in polymers

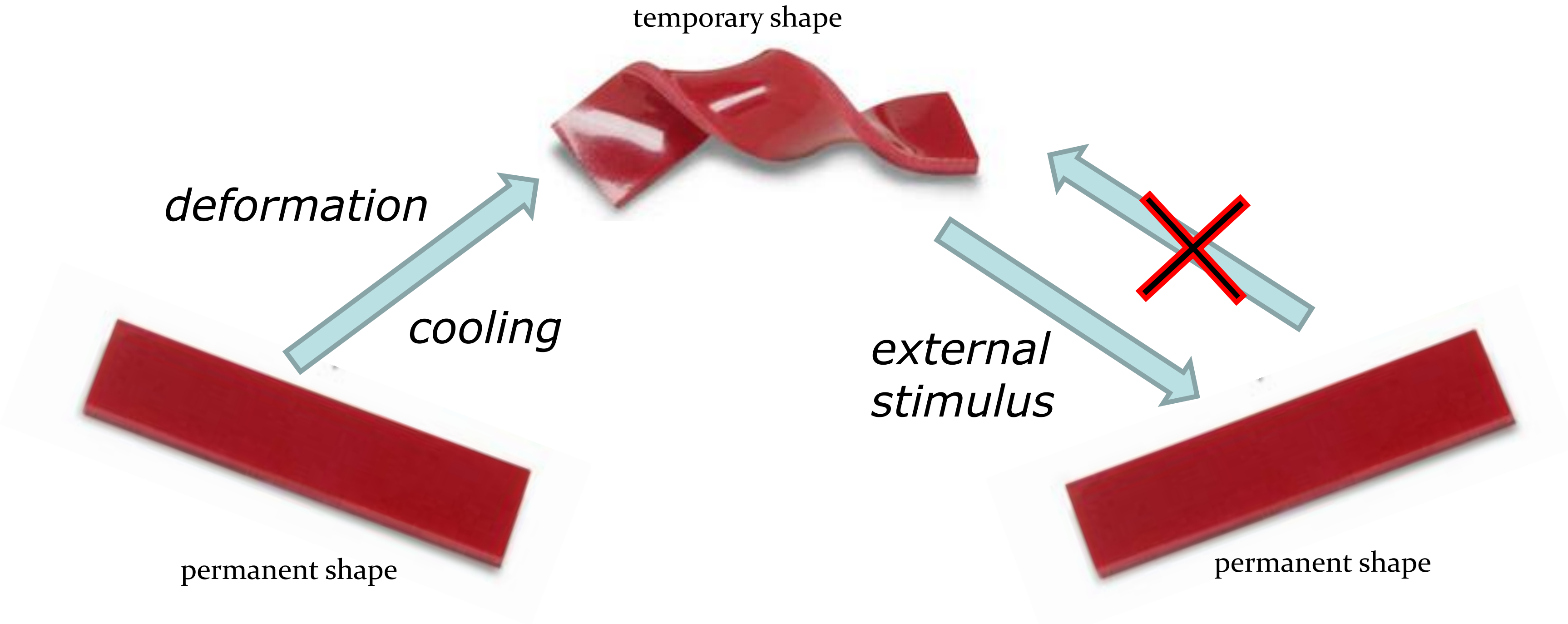
polymer structure

polymer morphology

polymer
processing technology

Shape memory can be observed for several polymers
which can differ even in their chemical composition and structure!

Shape memory effect in polymers



ONE-WAY SHAPE MEMORY EFFECT!

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A transparência é a nossa assinatura

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PORTUGUESA
FILMES BIORIENTADOS SA

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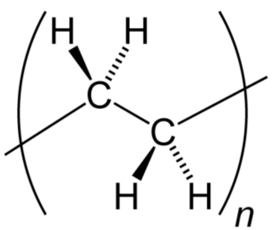
Multi-Purpose Shrink Film

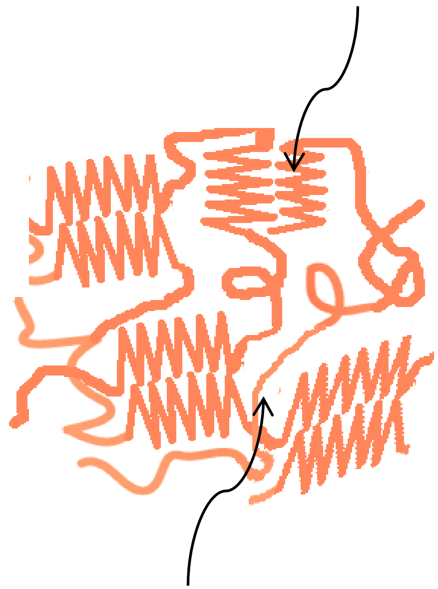
Exlfilm® *FPLL*, can be used for most general applications requiring durability. ***FPLL*** is a non-crosslinked film that is ideal for applications where products with "sharp" edges or corners are shrink-wrapped and/or products need extra protection. It has excellent optics and is extremely strong with seals at the same time. The film has a high burn-through resistance and has high hot-slip characteristics. Ideal products for **Exlfilm®** ***FPLL*** are: Do-It-Yourself products, mirrors, picture frames, wood products and long profiles.

Performance Features Equal Customer Value

POLYETHYLENE



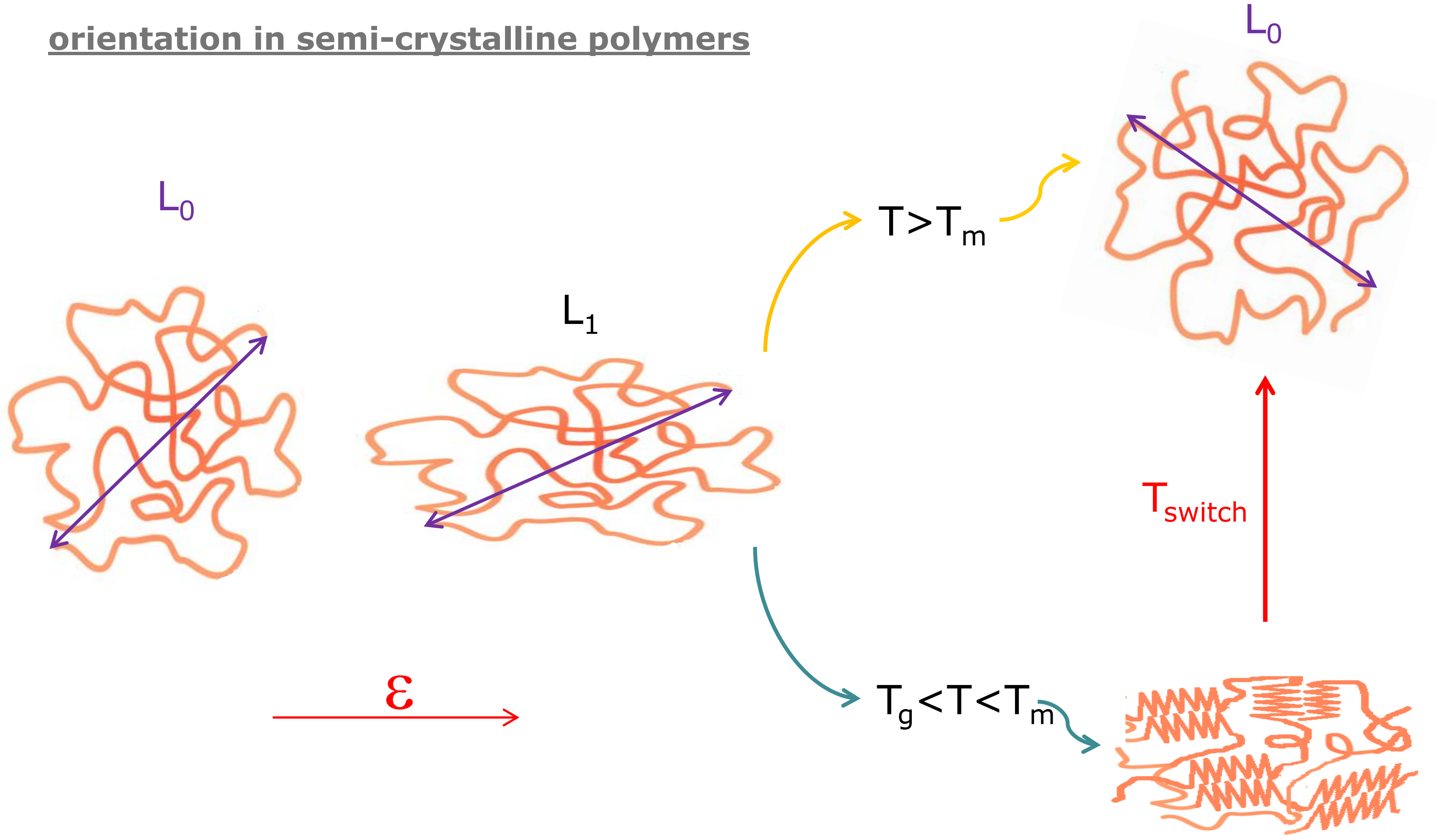
crystalline phase



amorphous phase

$T_m = 112°C$

orientation in semi-crystalline polymers

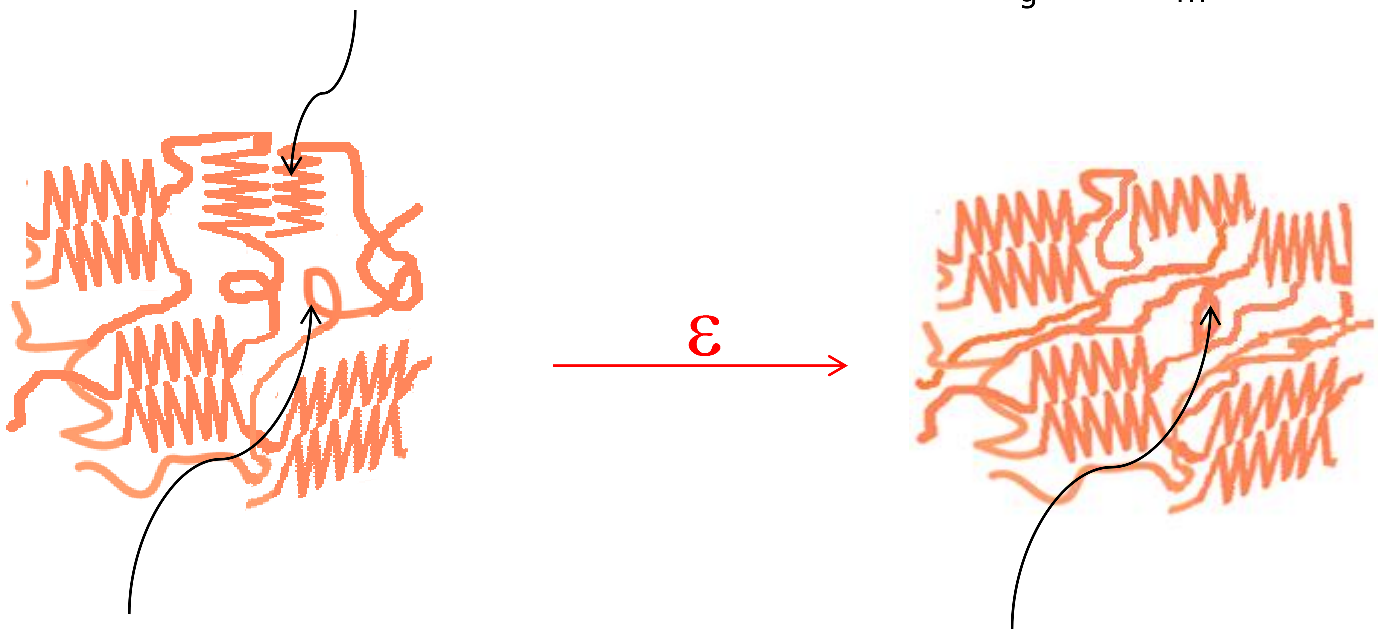


thermo-retraction and shape memory

cold-drawing process → orientation realized under isothermal condition (below the melting temperature)

crystalline phase

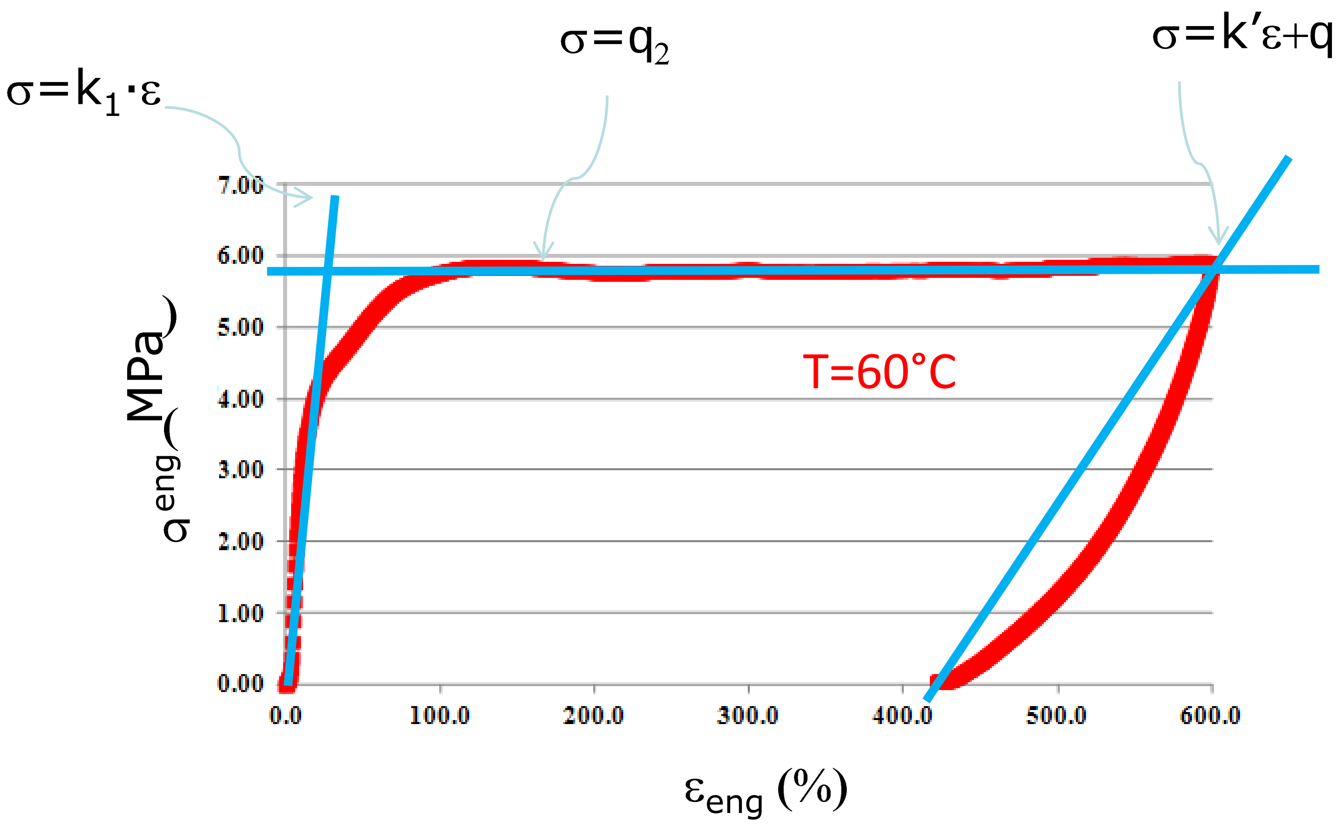
$T_g < T < T_m$



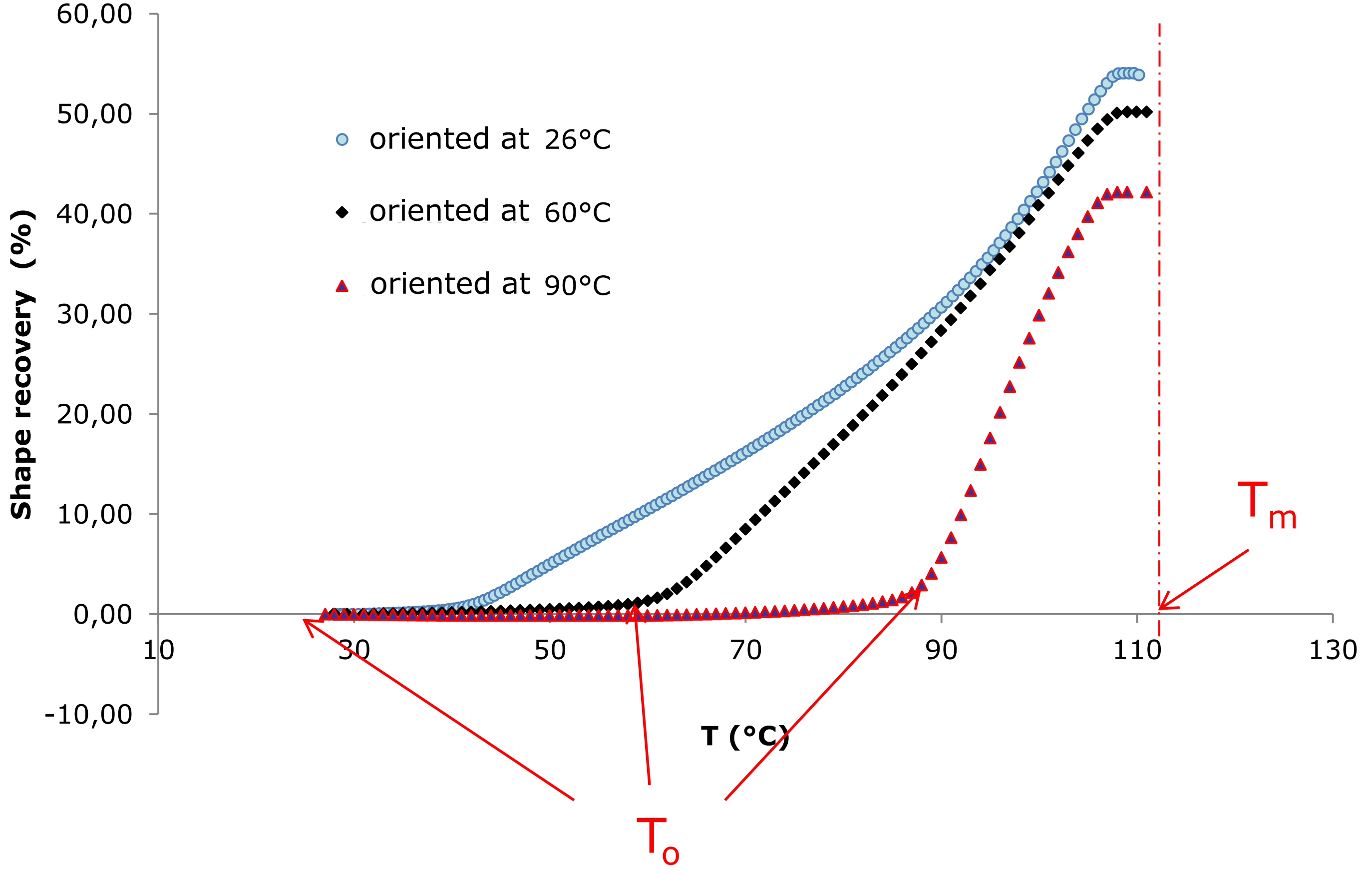
relaxed amorphous phase

oriented amorphous phase

cold-drawing process → orientation realized under isothermal condition (below the melting temperature)



free thermal shrinkage



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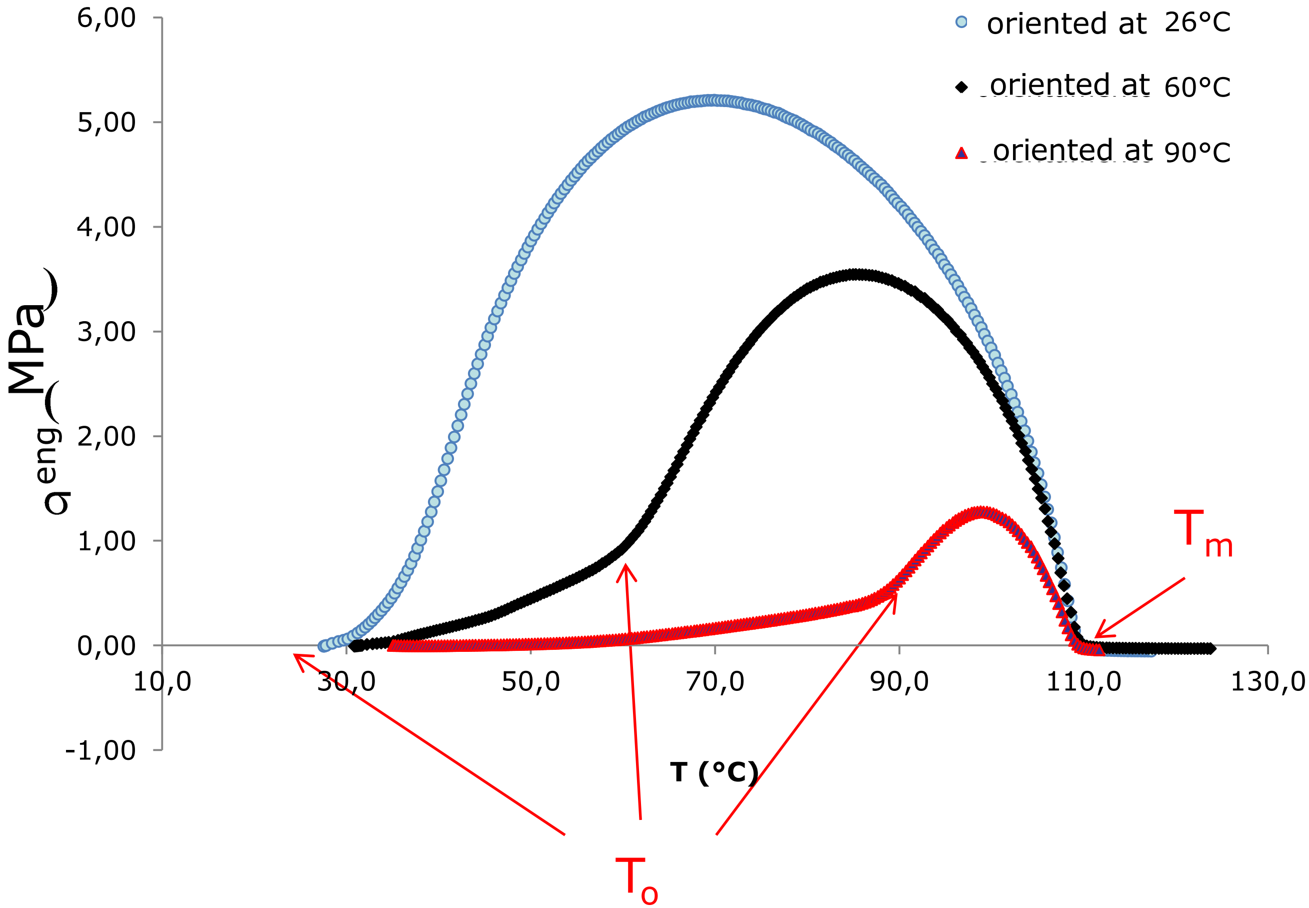
shrinkage force



PHASE TRANSITION MODEL

state variables

- θ ⟹ absolute temperature
- ε ⟹ deformation
- χ ⟹ phase parameter

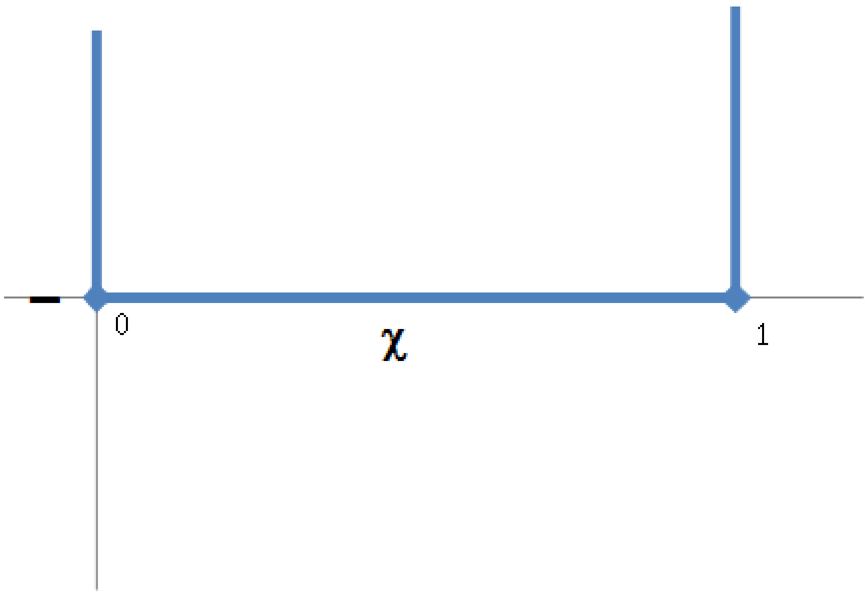
$$\chi \in [\,0\,,\,1\,]$$

0 → oriented phase

1 → non-oriented phase

$$\Psi(\theta,\chi,\varepsilon) = -c_s\theta\log\theta + \frac{1}{2}k(\theta,\chi)(\varepsilon + \tilde{q}(\theta,\chi))^2 + \lambda(\theta)\chi + I_{[0,1]}(\chi)$$

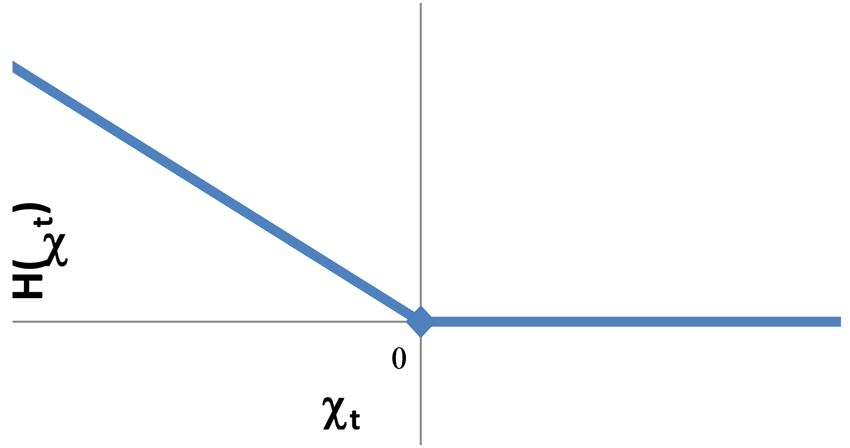
$$\begin{cases} I_{[0,1]}(\chi) = 0 \text{ if } \chi \in [0,1] \\ I_{[0,1]}(\chi) = +\infty \text{ if } \chi \notin [0,1] \end{cases}$$



$$\sigma = \frac{\partial\Psi}{\partial\varepsilon} = k(\theta,\chi)(\varepsilon + \tilde{q}(\theta,\chi))$$

$$\Phi(\theta, \chi_t) = H(\theta, \chi_t)$$

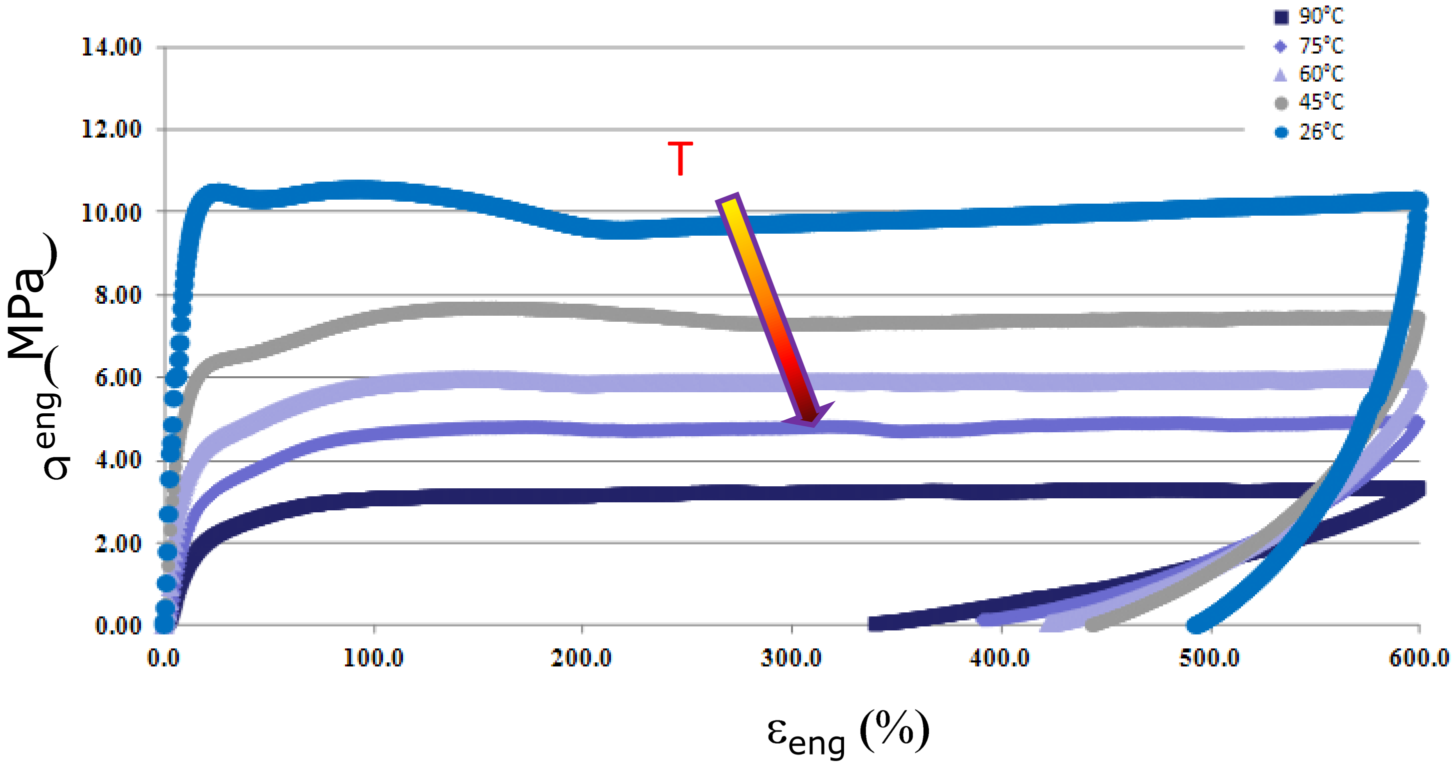
$$\begin{cases} H(x,y) = -\eta(x)y & \text{if } y \leq 0 \\ H(x,y) = 0 & \text{if } y \geq 0 \end{cases}$$



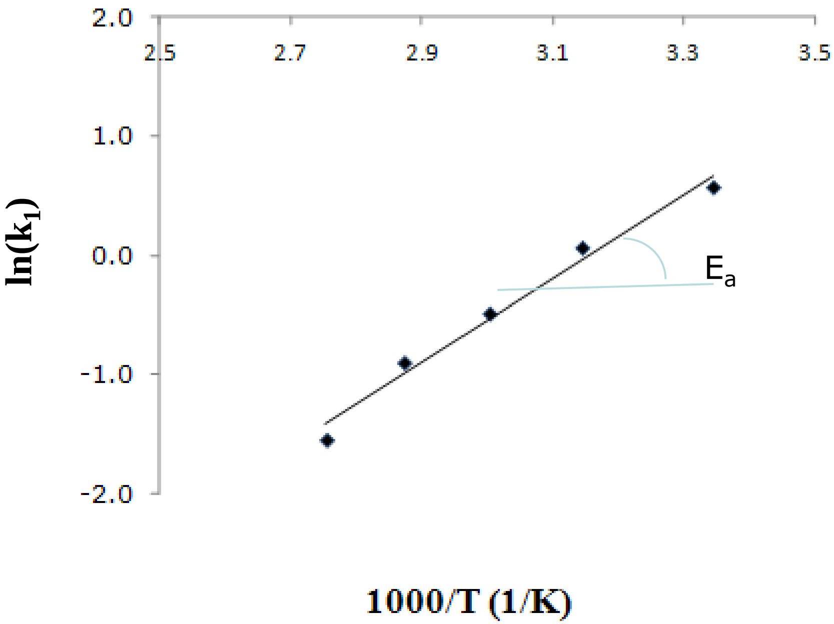
$$B = B^{nd} + B^{d} = \frac{\partial \Psi}{\partial \chi} + \frac{\partial \Phi}{\partial \chi_t}$$

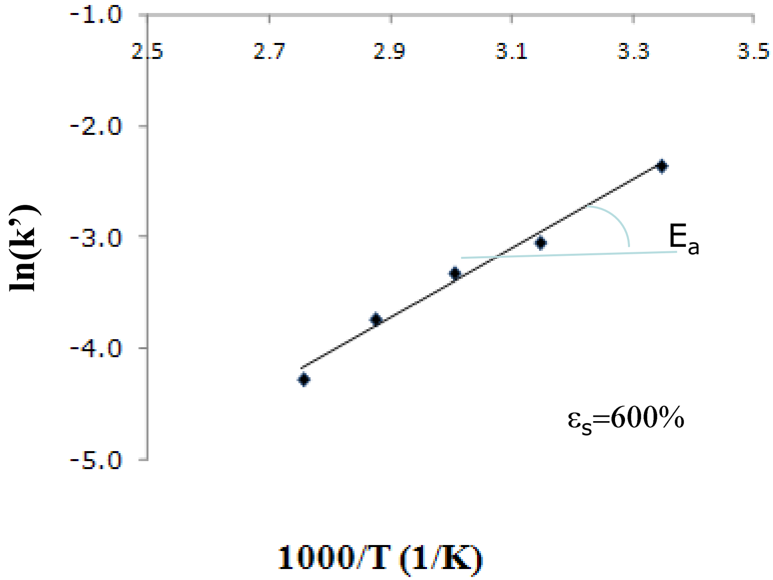
$$B = \frac{\partial H(\theta, \chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi) + \frac{1}{2}\frac{\partial k}{\partial \chi}(\boldsymbol{\varepsilon} + \widetilde{q}(\theta, \chi))^2 + k(\theta, \chi)\frac{\partial \widetilde{q}}{\partial \chi}(\boldsymbol{\varepsilon} + \widetilde{q}(\theta, \chi))$$

temperature effect

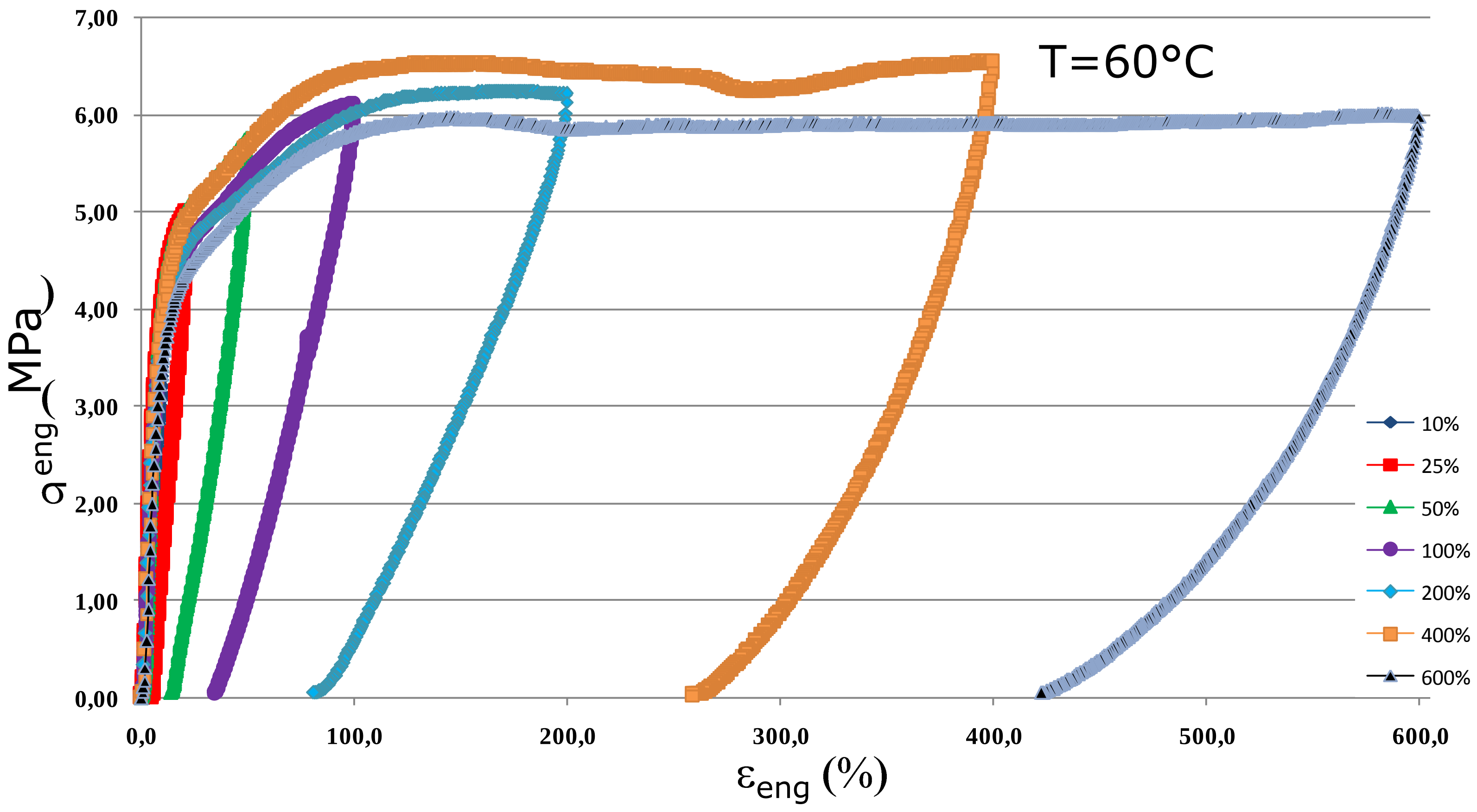


temperature effect

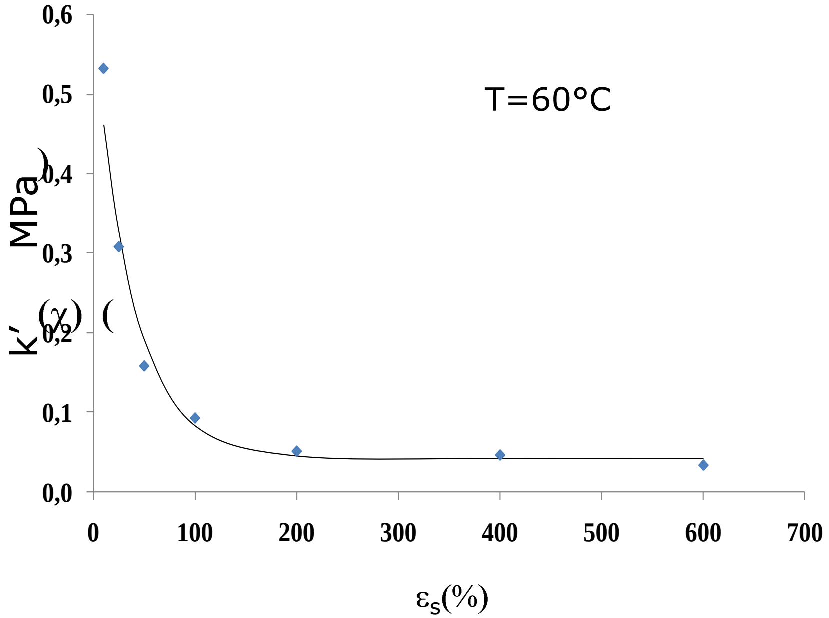


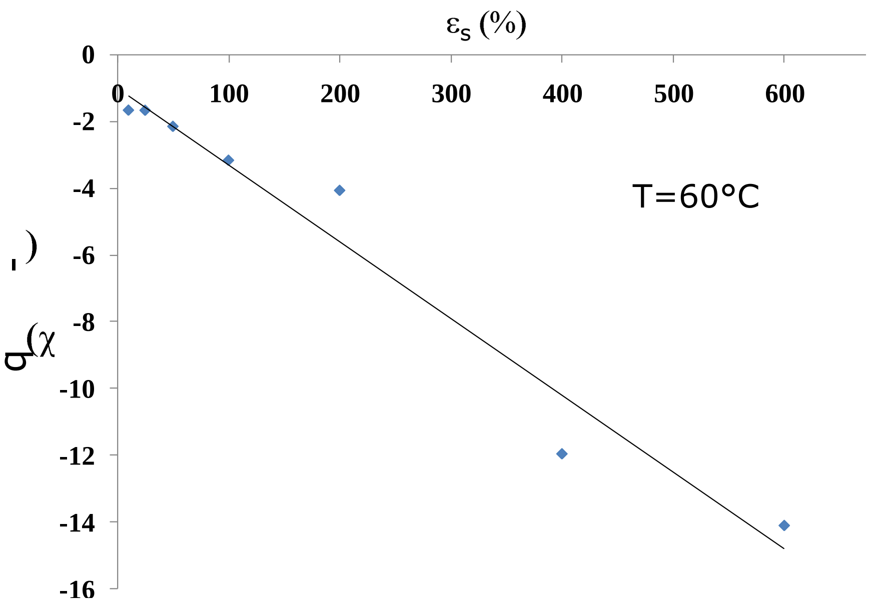


maximum deformation effect



maximum deformation effect





$$\boldsymbol{\sigma} = \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}} = k(\theta, \chi)(\boldsymbol{\varepsilon} + \widetilde{q}(\theta, \chi))$$

$$\begin{cases} k(\theta, \chi) = e^{\frac{E_a}{\theta}} \dfrac{1}{\frac{\chi}{k_1} + \frac{1-\chi}{k_2}} \\ \widetilde{q}(\theta, \chi) = -Ce^{\frac{E_a}{\theta}}(1-\chi), \quad q(1) = 0 \end{cases}$$

$$\sigma = e^{\frac{E_a}{\theta}} \frac{1}{\frac{\chi}{k_1} + \frac{1-\chi}{k_2}} (\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\chi))$$

$$\Phi(\theta, \chi_t) = H(\theta, \chi_t) \qquad \begin{cases} H(x,y) = -\eta(x)y & \text{if } y \leq 0 \\ H(x,y) = 0 & \text{if } y \geq 0 \end{cases}$$

$$B = \frac{\partial H(\theta, \chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi) + \frac{1}{2}\frac{\partial k}{\partial \chi}\frac{1}{k^2(\theta,\chi)}\sigma^2 - Cq'(\chi)\sigma$$

$$\begin{cases} k(\theta,\chi) = e^{\frac{E_a}{\theta}} \dfrac{1}{\frac{\chi}{k_1} + \frac{1-\chi}{k_2}} \\ \tilde{q}(\theta,\chi) = -Ce^{\frac{E_a}{\theta}}(1-\chi), \quad q(1) = 0 \end{cases}$$

$$\frac{\partial H(\theta, \chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi)$$

$$\ni -\frac{1}{2}e^{\frac{E_a}{\theta}}\frac{k_1 k_2 (k_1 - k_2)}{(k_2\chi + k_1(1-\chi))^2}(\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\chi))^2 - Ce^{\frac{2E_a}{\theta}}\frac{1}{\frac{\chi}{k_1} + \frac{1-\chi}{k_2}}(\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\chi))$$

$$\begin{cases} \chi = 1 \\ \boldsymbol{\varepsilon} = 0 \end{cases}$$

$$\longrightarrow \quad \sigma = e^{\frac{E_a}{\theta}} k_1 \boldsymbol{\varepsilon}$$

$$\frac{\partial H(\theta, \chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi)$$

$$\ni -\frac{1}{2} e^{\frac{E_a}{\theta}} \frac{k_1 k_2 (k_1 - k_2)}{(k_2 \chi + k_1 (1-\chi))^2} (\boldsymbol{\varepsilon} - C e^{\frac{E_a}{\theta}} (1-\chi))^2 - C e^{\frac{2E_a}{\theta}} \frac{1}{\frac{\chi}{k_1} + \frac{1-\chi}{k_2}} (\boldsymbol{\varepsilon} - C e^{\frac{E_a}{\theta}} (1-\chi))$$

$$\longrightarrow \quad \chi_t \leq 0$$

$$\chi \in [0,1]$$

$$\longrightarrow \quad \sigma = e^{\frac{E_a}{\theta}} k_1 \boldsymbol{\varepsilon}_y = q_2(\theta)$$

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_s, \qquad \textit{unloading phase}$$

$$\frac{\partial H(\theta,\chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi)$$

$$\ni -\frac{1}{2}e^{\frac{E_a}{\theta}}\frac{k_1k_2(k_1-k_2)}{(k_2\chi + k_1(1-\chi))^2}(\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\chi))^2 - Ce^{\frac{2E_a}{\theta}}\frac{1}{\frac{\chi}{k_1}+\frac{1-\chi}{k_2}}(\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\chi))$$

$$\longrightarrow \chi_t = 0$$

$$\longrightarrow \sigma = e^{\frac{E_a}{\theta}}\frac{1}{\frac{\widehat{\chi}}{k_1}+\frac{1-\widehat{\chi}}{k_2}}(\boldsymbol{\varepsilon} - Ce^{\frac{E_a}{\theta}}(1-\widehat{\chi}))$$

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$$\begin{cases} \chi \in [0,1] \\ \sigma = 0 \end{cases}$$

$$\frac{\partial H(\theta, \chi_t)}{\partial \chi_t} + \partial I_{[0,1]}(\chi)$$

$$\ni 0$$

$$\longrightarrow \chi_t \geq 0$$

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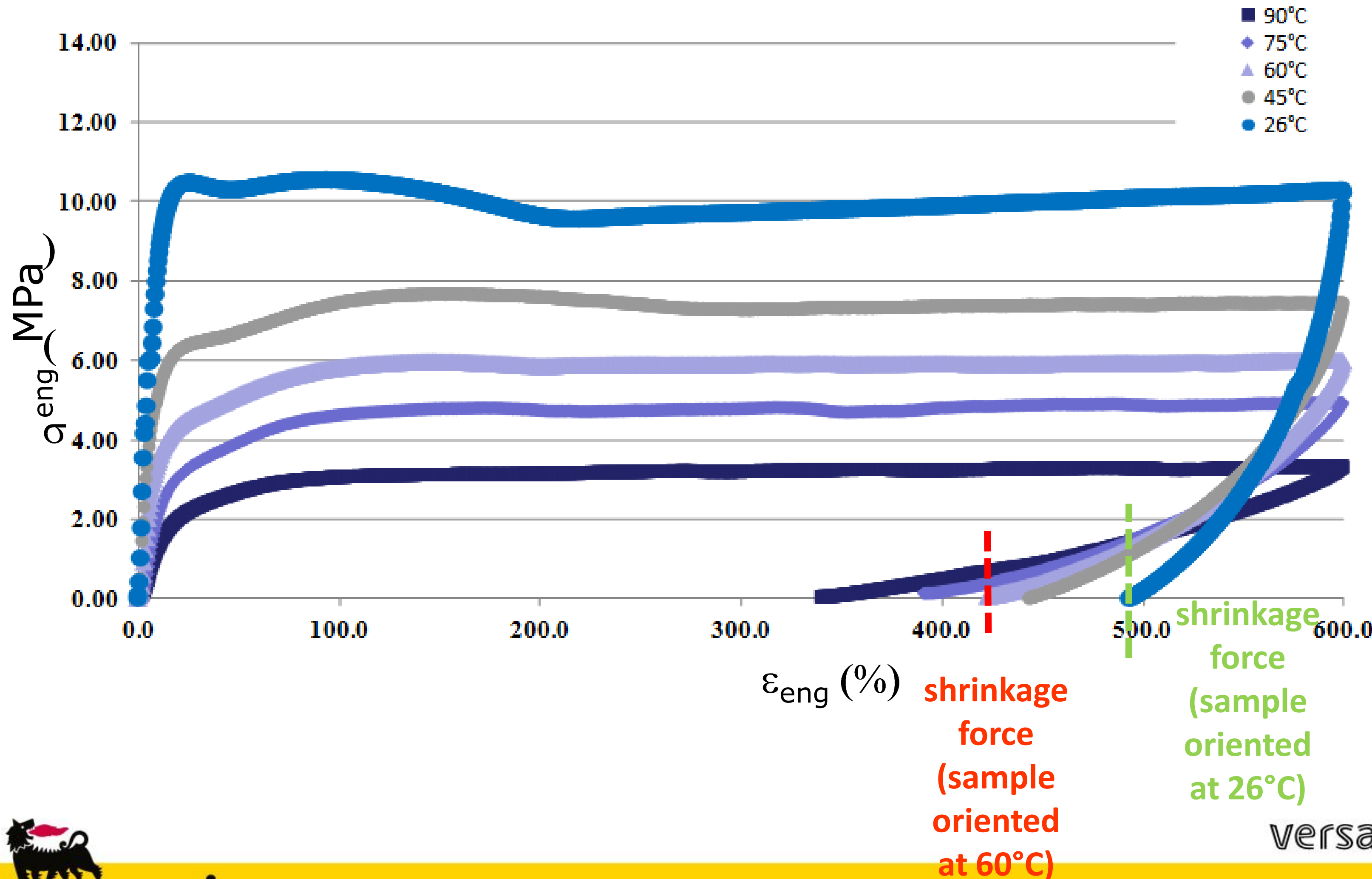
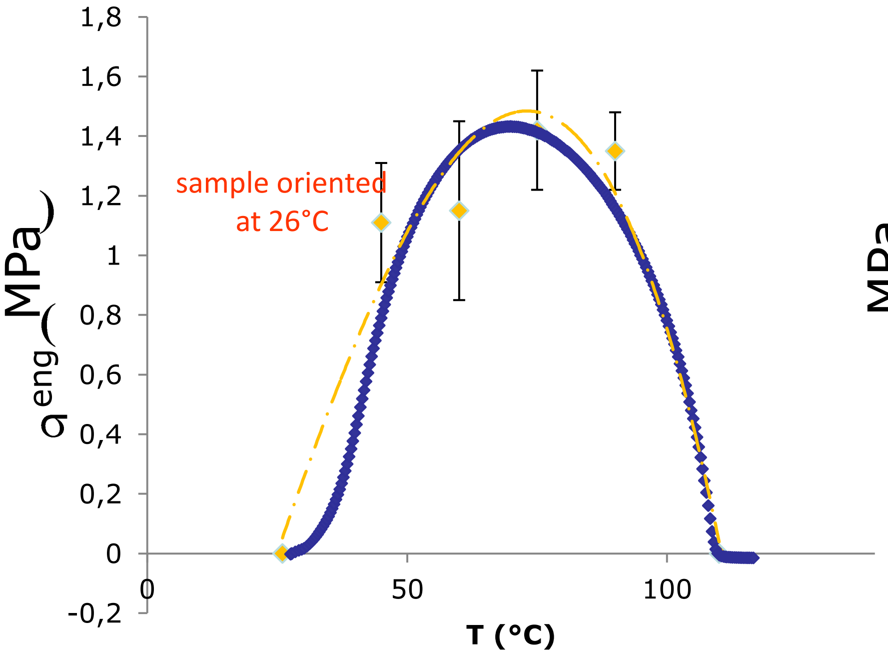
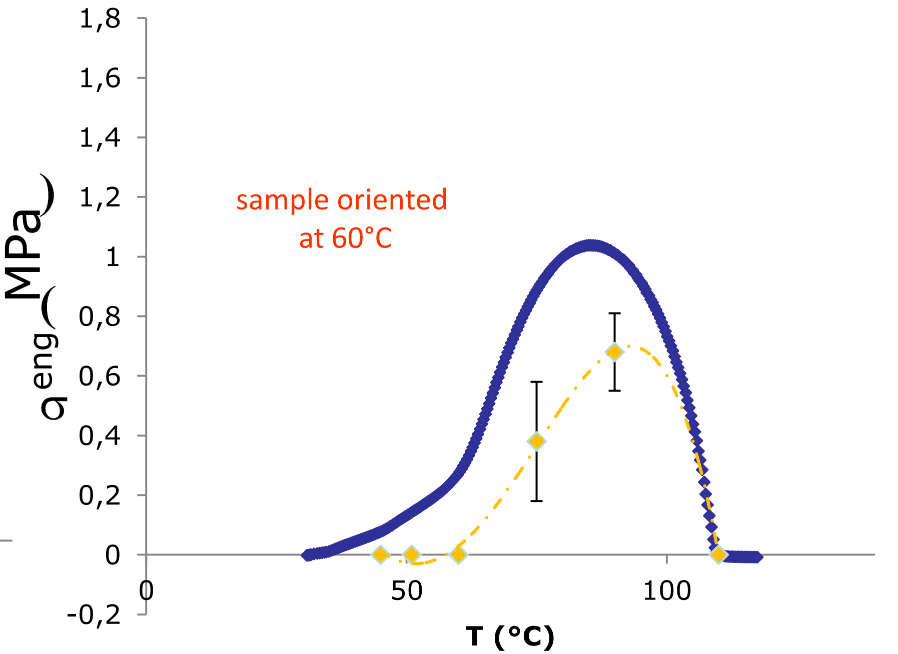
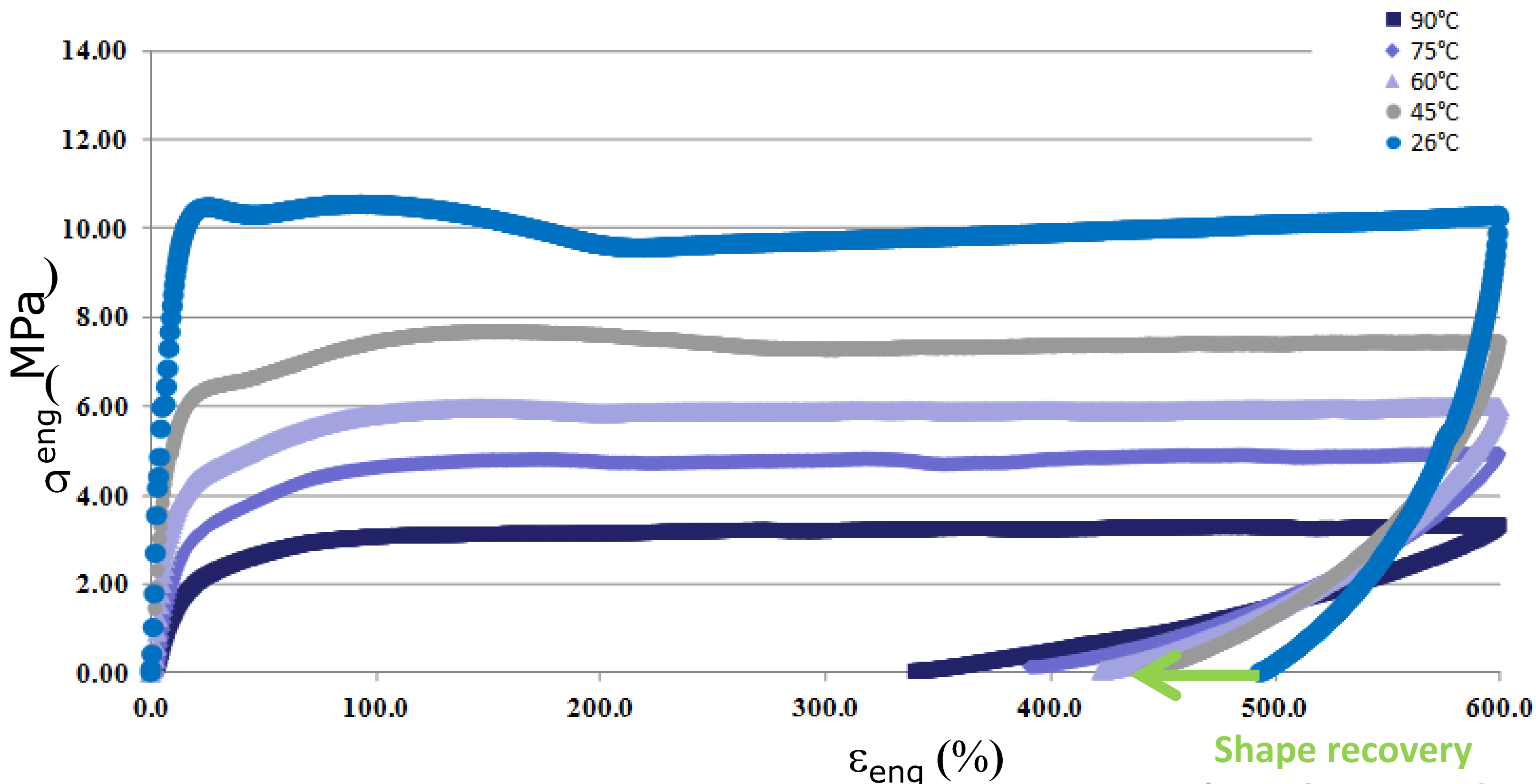

90°C
75°C
60°C
45°C
26°C
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
σeng (MPa)
0.0
100.0
200.0
300.0
400.0
500.0
600.0
εeng (%)
shrinkage force (sample oriented at 60°C)
shrinkage force (sample oriented at 26°C)

Comparison with experimental results

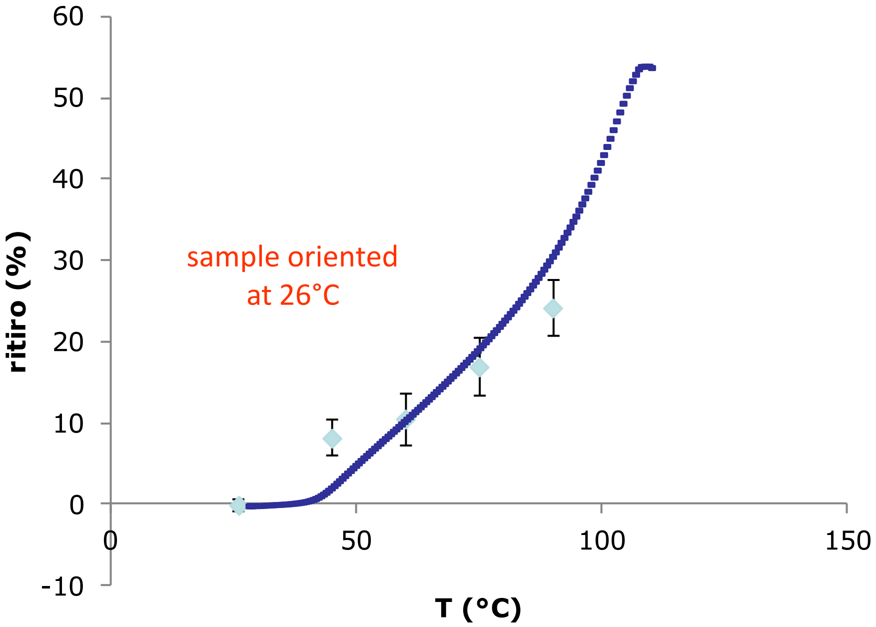


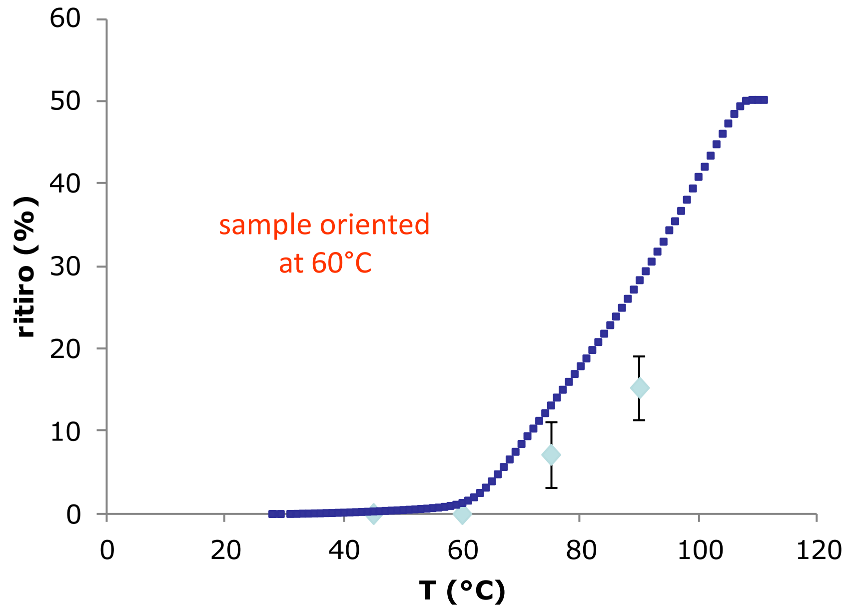




Shape recovery (sample oriented at 26°C)

Comparison with experimental results





- Semi-crystalline polymeric materials show thermal retraction on heating when the molecular structure has been oriented.
- Thermal retraction can be interpreted as a “shape memory behavior”.
- A one-dimensional thermo-mechanical model has been developed using the "phase transition" approach .
- A set of parameters capable of describing the mechanical behavior of the material has been identified.
- A good agreement between prediction and experiments has been found.